THE NEW QUANTUM THEORY AND THE ZEEMAN EFFECT

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1. The treatment of the Zeeman effect from the point of view of Schroedinger's theory presents certain difficulties. Let us consider the case of a hydrogen atom in a homogeneous magnetic field of the strength **H**. We start from the customary expressions of the Hamiltonian function for this case, and derive from it the fundamental wave equation by the procedure given by Schroedinger[1] and independently by Eckart.[2] The result is the equation given explicitly by Eckart

$$\nabla^2\psi + \frac{e}{ick}\,\mathbf{H}\cdot(\mathbf{r}\times\nabla\psi) + \frac{2\mu}{k^2}\left(E + \frac{e^2}{r}\right)\psi = 0, \qquad (1)$$

e and μ denote the charge and mass of an electron, c the velocity of light, E the energy constant, k is an abbreviation for $h/2\pi$ (h Planck's constant) and the vector $\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z$.

If we introduce a system of polar coördinates r, ϑ, φ, taking the direction of the magnetic field as the polar axis, the equation becomes

$$[\psi] + \frac{1}{r^2\sin^2\vartheta}\frac{\partial^2\psi}{\partial\varphi^2} + \frac{eH}{ick}\frac{\partial\psi}{\partial\varphi} = 0, \qquad (2)$$

with the abbreviation

$$[\psi] = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial\psi}{\partial\vartheta}\right) + \frac{2\mu}{k^2}\left(E + \frac{e^2}{r}\right)\psi. \qquad (3)$$

The difficulty above mentioned lies in the fact that the term with $\partial\psi/\partial\varphi$ is imaginary. Formally the equation can be solved by substituting $\psi = \psi'$ exp. $(\pm i\tau\varphi)$. This even leads to energy levels identical with those of the old theory, but the factor exp. $(\pm i\tau\varphi)$ does not represent a standing wave required by Schroedinger's theory. If we take into account the time factor exp. $(i\omega t)$ of the partial oscillations ($\omega = 2\pi\nu$), we get the factor exp. $(i\omega t \pm i\tau\varphi)$, which represents a progressing wave winding itself around the polar axis at the very high angular velocity ω/τ.

That this is impossible becomes apparent also from the following consideration. Before subjecting the Hamiltonian function to the Schroedinger procedure, we could have transformed it by introducing rotating axes of coördinates. If the rotation is that of the Larmor precession, the transformed Hamiltonian function is identical with that of a resting hydrogen atom not acted upon by a magnetic field. Since the Hamiltonian function defines Schroedinger's wave equation, we see, carrying out this process, that in the Zeeman effect the system of standing waves is the same for the rotating observer as in the simple case without a magnetic field for the resting observer. In other words, if we subject the wave system, existing in the simple case, to a Larmor precession, we obtain the solution in the case of the Zeeman effect. Our difficulty can now be stated by the following question: Why cannot we reverse the order of operations? Why is it, that carrying out the Schroedinger process first, we find equation (1) whose solution has nothing to do with that stated above? We shall see in the following sections that equation (1) is incorrect and that the problem must be approached in a different way.

2. It appears that the difficulty stated in section 1 is not a new one, but only an aggravated form of an old trouble of the theory of the Zeeman effect under which it labored from the very beginning of the quantum theory. The magnetic forces are not conservative and the integration constant of the dynamical equations for a system moving in a magnetic field does not represent the whole of the magnetic energy. Early workers in this field were puzzled why, taking into account only this part of the energy, they were led to correct results. It was pointed out by H. A. Lorentz[3] that one can get around the difficulty by extending the system under consideration and by including into it the source of the magnetic field. The extended system will obey the law of conservation of energy and the ambiguity will be removed. We shall show that Lorentz's suggestion solves also the discrepancy in our case.

Let us use as the source of our magnetic field a current $\dot{J}$ moving, without resistance, in a closed linear conductor of uniform cross-section. We denote by q the position of a chosen particle of charge in this conductor and by $\dot{q}$ the uniform velocity of all the charges in it. If the linear density of charge is ρ and the coefficient of self-induction L, we have $J = \rho\dot{q}$, while the energy of the current is

$$LJ^2/2 = L\rho^2\dot{q}^2/2. \tag{4}$$

Denoting for short by T and U the kinetic and potential energy of the electron in our hydrogen atom, we have for the total kinetic potential of the system, neglecting the interaction between atom and current,

$$K_0 = T + L\rho^2\dot{q}^2/2 - U. \tag{5}$$

To this must be added the contribution of the interaction. The electron moves with the velocity $\mathbf{v}$ in the magnetic field of the current, which can be described by the vector potential $\mathbf{A}$. This gives rise to the term $K' = -e(\mathbf{v}\cdot\mathbf{A})/c$. We could write for the vector potential $\mathbf{A} = \dot{q}\mathbf{A}_1$, where the vector $\mathbf{A}_1$ is independent of $\dot{q}$. Similarly we can write for the strength of field $\mathbf{H} = \dot{q}\mathbf{H}_1$, with the relation $\mathbf{H}_1 = \nabla \times \mathbf{A}_1$. Moreover, making use of the indeterminateness of the vector potential, we subject it to the conditions: $\mathbf{A}_1 = 0$, in the position of the nucleus, and $\nabla \cdot \mathbf{A}_1 = 0$, generally. Finally, we must remember that we are dealing with the case that the field can be regarded as homogeneous over the size of the atom, so that $\mathbf{H}_1$ is constant and $\mathbf{A}_1 = (\mathbf{H}_1 \times \mathbf{r})/2$. Therefore, we have

$$K' = -e\mathbf{v}\cdot(\mathbf{H}_1 \times \mathbf{r})\dot{q}/2c = e\mathbf{H}_1\cdot(\mathbf{r} \times \mathbf{v})\dot{q}/2c.$$

On the other hand the current is flowing in the magnetic field of the electron. It is, however, well known that this fact does not involve a new term in the kinetic potential. It only leads to a different formulation of K' and is taken care of by this term. The complete kinetic potential is, therefore,

$$K = \mu v^2/2 + L\rho^2\dot{q}^2/2 + e\mathbf{H}_1\cdot(\mathbf{r} \times \mathbf{v})\dot{q}/2c. \tag{6}$$

3. Deriving from this the momenta and the Hamiltonian function in the usual way, we find

$$\mathbf{p} = \mu\mathbf{v} - e(\mathbf{r} \times \mathbf{H}_1)\dot{q}/2c, \qquad p_q = L\rho^2\dot{q} + e\mathbf{H}_1\cdot(\mathbf{r} \times \mathbf{v})/2c, \tag{7}$$

denoting by $\mathbf{p}$ the vector $\mathbf{p} = \mathbf{i}p_x + \mathbf{j}p_y + \mathbf{k}p_z$

$$H = \mathbf{p}^2/2\mu + p_q^2/2L\rho^2 - e\mathbf{H}_1\cdot(\mathbf{r} \times \mathbf{p})p_q/2L\rho^2\mu c + U, \tag{8}$$

neglecting terms of the second order in $\mathbf{H}_1$.

We derive from this expression the wave equation by the Schroedinger variation process[4]

$$\nabla^2\psi + \frac{\mu}{L\rho^2}\frac{\partial^2\psi}{\partial q^2} - e(\mathbf{H}_1 \times \mathbf{r})\cdot\nabla\frac{\partial\psi}{\partial q}/L\ \rho^2 c + \frac{2\mu}{k^2}(E-U)\psi = 0. \tag{9}$$

If we substitute polar coördinates, choosing the direction of the vector $\mathbf{H}_1$ as the polar axis, this becomes

$$[\psi] + \frac{1}{r^2\sin^2\vartheta}\frac{\partial^2\psi}{\partial\varphi^2} - \frac{eH_1}{L\rho^2 c}\frac{\partial^2\psi}{\partial\varphi\partial q} + \frac{\mu}{L\rho^2}\frac{\partial^2\psi}{\partial q^2} = 0. \tag{10}$$

This is the fundamental equation of our problem and it is entirely different from equation (2). We can easily reduce it to a separable form by using instead of φ a new variable φ' defined by

$$\varphi = \varphi' + q\ eH_1/2\mu c. \tag{11}$$

The substitution gives

$$[\psi] + \frac{1}{r^2}\frac{1}{\sin^2\vartheta}\frac{\partial^2\psi}{\partial\varphi'^2} + \frac{\mu}{L\rho^2}\frac{\partial^2\psi}{\partial q^2} = 0. \tag{12}$$

The term depending on the magnetic field has disappeared, and (12) is formally identical with the equation for the case of a hydrogen atom and current which do *not* react on each other. Because of this absence of interaction, we can leave the variable q out and treat the phenomena in the space r, ϑ, φ' separately. The problem is then formally identical with that of the unperturbed hydrogen atom in the space r, ϑ, φ. This problem was solved by Schroedinger[4] and all his results are immediately applicable in our case, we need only to substitute everywhere φ' instead of φ. Especially, we must note that the optical frequencies are identical in both cases.

4. Let us now discuss how the phenomena appear in the real physical space. What is the physical meaning of transformation (11)? Since, within the approximation here required, the velocity $\dot{q}$ of the electric charges in our conductor is constant, we have $q = \dot{q}t$, and we had defined $H = H_1\dot{q}$. This gives

$$\varphi = \varphi' + eHt/2\mu c, \tag{13}$$

the familiar expression of the Larmor precession.

We see, therefore, that the discrepancy stated in section 1 is removed. The order of the two operations, introduction of rotating axes of coördinates and Schroedinger procedure, is interchangeable. Both ways we get the same solution of the problem. It hardly is necessary to add that this theory gives the Lorentz triplet and equal intensities for all three components of it.

Equation (2) is incorrect because it is based on the consideration of only a part of our energetic system. It could be obtained from (10) by the assumption of a very special complex dependence of ψ on q, which, without any doubt, is not justified because it does not give standing waves in the r, ϑ, φ', q space.

5. The considerations of the preceding sections suggest a method of extending the Schroedinger-Eckart procedure to the general case of any Hamiltonian system. These authors state their rule for systems subject to the equation (q coördinates of position),

$$H(p, q) - E = 0, \tag{14}$$

in the following form: Substitute in H instead of the momenta p the symbols $ik\partial/\partial q$ and regard H-E as an operator operating on the function ψ. The result is Schroedinger's wave equation in the form

$$[H(ik\partial/\partial q, q) - E]\psi = 0. \tag{15}$$

The rule is enunciated only for Hamiltonian functions not containing the time explicitly, and we have seen that, even in some of these special cases, it fails.

Let us now take the general form of the Hamiltonian equation,

$$H(p, q, t) + \partial S/\partial t = 0. \tag{16}$$

The mathematical beauty of the Hamiltonian theory lies mainly in the fact that the variables of position q and the time t are treated exactly in the same way. From the mathematical point of view the partial $\partial S/\partial t$ is nothing but another momentum p_t. It seems, therefore, logical to make for it the same substitution as for the rest of the momenta. The generalized equation we propose is, consequently,

$$[H(ik\partial/\partial q, q, t) + ik\partial/\partial t]\psi' = 0. \tag{17}$$

For instance, in the case of a single electron in a field of conservative forces, this gives

$$\nabla^2\psi' - \frac{2\mu}{k^2} U\psi' + \frac{2\mu}{ik}\frac{\partial\psi'}{\partial t} = 0. \tag{18}$$

We see that Schroedinger's equation, generalized to include the time, does not contain the second derivative with respect to time, but the first. It is, technically speaking, not a wave equation, as he expected it to be, but an equation of conduction with an imaginary conductivity. If we substitute the usual form of the time factor $\psi' = \psi$ exp. $(2\pi i\nu t)$, the result is

$$\nabla^2\psi + \frac{2\mu}{k^2}(h\nu - U)\psi = 0. \tag{19}$$

Comparing with the form (14) we find

$$E = h\nu.$$

This relation, surmised also by Schroedinger, seems to follow in a much more direct and convincing way from our assumption than from Schroedinger's ingenious argumentation.

Our rule stands, also, the test of the Zeeman effect. Equation (2) of section 1 must be replaced now by

$$\nabla^2\psi' + \frac{eH}{ick}\frac{\partial\psi'}{\partial\varphi} + \frac{2\mu}{ik}\frac{\partial\psi'}{\partial t} - \frac{2\mu}{k^2} U\psi' = 0. \tag{20}$$

Substitution (13) transforms this equation into the form (18) with the only difference that it is expressed in the coördinates r, ϑ, φ' instead of r, ϑ, φ. Again we find that the action of a magnetic field is equivalent to a Larmor precession, so that all the conclusions of section 4 hold also for this treatment. It is remarkable that the solution so obtained is rigorous: no terms of the second order are neglected, as in the old theory.

[1] E. Schroedinger, *Ann. Physik*, **79**, p. 745 (1926).

[2] C. Eckart, *Physik. Rev.*, October, 1926.

[3] H. A. Lorentz, "Problems of Modern Physics."

[4] E. Schroedinger, *Ann. Physik*, **79**, p. 361 (1926).